



## Short communication

## A novel polymer composite as cathode binder of lithium ion batteries with improved rate capability and cyclic stability



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## H I G H L I G H T S

- Composite of MA-g-PVDF with PVDF was developed as binder for LiCoO<sub>2</sub> cathode of lithium ion battery.
- Composite exhibits lower crystallinity than PVDF and increases electrolyte uptake of cathode.
- Application of composite improves significantly rate capability and cyclic stability of battery.

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## A B S T R A C T

In this work, we have developed a novel polymer composite (MPVDF) by embedding maleic anhydride-grated-polyvinylidene fluoride (MA-g-PVDF) into polyvinylidene fluoride (PVDF) as binder of LiCoO<sub>2</sub> cathode for lithium ion battery. The cathodes using MPVDF and PVDF as binder have been comparatively investigated with scanning electron microscope (SEM), X-ray diffraction (XRD) and electrochemical measurements. By using MPVDF as the binder for preparing LiCoO<sub>2</sub> cathode, the rate capability and cyclic stability of the LiCoO<sub>2</sub> cathode in LiCoO<sub>2</sub>/Artificial graphite battery are improved significantly. Compared to the cathode using PVDF alone, the discharge capacity of the battery increases by 38.5% at 2 C and the capacity retention of the battery is improved from 84.5% to 90.2% after 300 cycles at 0.5 C when the mass ratio of MA-g-PVDF to PVDF in MPVDF binder is 1:4. The improved performance is attributed to the low crystallinity of MPVDF, which allows larger electrolyte uptake. The electrolyte uptake is 43.5% for the LiCoO<sub>2</sub> cathode using MPVDF but only 25.3% for the cathode using PVDF alone.

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## 1. Introduction

Compared to other electrochemical energy storage technologies, lithium ion batteries offer the best promises for many applications, because of their high energy density and power density, and long-term duration [1–4]. A typical lithium ion battery consists of a graphite anode, a transition metal oxide (such as LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub> and LiNiO<sub>2</sub>) cathode, separator and a non-aqueous organic electrolyte [5,6]. LiCoO<sub>2</sub>, as the most successful commercial cathode

material, has been widely used in the lithium ion batteries due to its virtues such as easy preparation, structural stability and long cycle life [7,8], but the performance of the current LiCoO<sub>2</sub> based lithium ion battery is still not satisfying. To meet the high capacity and long cycle life requirements of lithium ion batteries for electrical vehicles and new electronic devices, many researchers are interested in the development of the cathodes with higher compacted density [9–11]. Although increasing the compacted density of the LiCoO<sub>2</sub> is supposed to be an effective way to increase the volume energy density of the battery, this strategy does not favor the electrolyte uptake and ion conduction inside the electrode, deteriorating rate capability and cyclic stability of the battery.

Matching the compacted density and electrolyte uptake remains a challenge for LiCoO<sub>2</sub> cathode. At present, the binder is dominated

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by polyvinylidene fluoride (PVDF) relying on its excellent electrochemical stability and binding capability [12–15]. However, PVDF does not favor electrolyte uptake. Fortunately, it has been found that the electrolyte uptake of PVDF can be greatly promoted by grafting [16,17]. However, this approach reduces the adhesion among cathode materials and between cathode materials and current collector.

With an aim to promote the electrolyte uptake without reducing the adhesion in the LiCoO<sub>2</sub> cathode, we introduced maleic anhydride-grated-polyvinylidene fluoride (MA-g-PVDF) with low crystallinity into PVDF as a composite binder of the cathode. Its effects on the rate capability and cyclic stability of LiCoO<sub>2</sub>/Artificial graphite battery were understood with the X-ray diffraction, cyclic voltammetry, scanning electron microscope, electrochemical impedance spectroscopy, and charge/discharge test.

## 2. Experimental

### 2.1. Materials

The cathode material used in this research was commercial LiCoO<sub>2</sub> powder from Shanshan Tech Co., Ltd, China. The average particle size is in the range of 13–18 μm, with the biggest size of less than 35 μm and the average specific area was in the range of 0.05–2.0 m<sup>2</sup> g<sup>−1</sup>. Maleic anhydride-grated-polyvinylidene fluoride (MA-g-PVDF) with an average molecular weight of 450,000 and PVDF with an average molecular weight of 1,000,000 were purchased from Arkema Shanghai Co., Ltd. Battery grade Super-P with an average particle size of 40 nm was acquired from MMM carbon, Belgium. Anhydrous 1-methylpyrrolidinone (NMP) was purchased from Dongguan Pengjin Chemical CO., Ltd. The artificial graphite with the particle size in the range of 13–20 μm was purchased from Shanshan Tech Co., Ltd. Carboxymethyl cellulose (CMC) was purchased from Foshan Rite Chemical Co., Ltd, China. Aqueous solution of 45% styrene-butadiene rubber (SBR) were obtained from Guangzhou Shuangri Co., Ltd, China. An electrolyte of 1 M LiPF<sub>6</sub> in EC:EMC:DMC, 1:1:1 by volume, was purchased from Shanshan Tech Co., Ltd, China. A PE separator of 16 μm thick was purchased from Foshan Jinhui Hi-Tech Optoelectronic Material Co., Ltd, China.

### 2.2. Electrode preparation

LiCoO<sub>2</sub> cathodes with MPVDF binder were prepared by mixing 96.5 wt% LiCoO<sub>2</sub>, 1.5 wt% MPVDF binder (MA-g-PVDF:PVDF = 1:4 and 1:2), and 2 wt% Super-p, in N-methyl-2-pyrrolidone, coating the mixture onto an aluminum foil current collector. The LiCoO<sub>2</sub> cathode with 1.5 wt% PVDF binder alone for comparison was also prepared with the same procedures. The graphite anode was prepared by mixing 95 wt% artificial graphite, 1.8 wt% CMC, 2.2 wt% SBR, and 1 wt% Super-P in aqueous solution, and coating the mixture onto a copper foil current collector. In the full cells, the compacted density of the LiCoO<sub>2</sub> cathode and anode is 4.15 g cm<sup>−3</sup> and 1.60 g cm<sup>−3</sup>, respectively, and the electrolyte is 5.15 g.

### 2.3. Electrode characterization

The morphology of the electrodes was imaged with a JEOL JEM-2100 field emission scanning electron microscope (SEM). The XRD patterns of the binders were obtained on a Rigaku D/max 2200 vpc diffractometer operated at 30 kV and 20 mA with Cu Kα radiation.

The electrolyte uptake (*A*) of the electrode films was determined by immersing the electrodes in the same electrolyte as used in battery for 24 h and calculated based on [18]:

$$A(\%) = (W_2 - W_1)/W_1 \times 100\% \quad (1)$$

where *W*<sub>1</sub> and *W*<sub>2</sub> are the mass of the dry and wet electrode films, respectively.

The adhesion of the cathode mixture with the current collector was estimated by a peel test on a RS-5 tensile tester. The LiCoO<sub>2</sub> cathodes were glued to the glass using double-sided adhesive and then tested with a peel speed of 250 mm min<sup>−1</sup>.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed in LiCoO<sub>2</sub>/Li coin cell on CHI660 (Chenhua, Shanghai). CV was carried out with a scanning rate of 0.1 mV s<sup>−1</sup> in the voltage range of 3.0–4.5 V and EIS was carried out with an amplitude of 10 mV from 100 KHz to 0.01 Hz.

The charge/discharge tests of battery were conducted on a Li-ion Battery Automatic Testing and Formation System (BK-3512L/2), using 18650 LiCoO<sub>2</sub>/Artificial graphite battery with nominal capacity of 2600 mAh. The battery was charged from 3.0 V to 4.2 V at a constant current of 1300 mA (0.5 C) and discharged at 0.2 C, 0.5 C, 1.0 C and 2.0 C. Internal resistance of the battery was also recorded in each cycle.

## 3. Results and discussion

### 3.1. Electrolyte uptake and adhesion strength

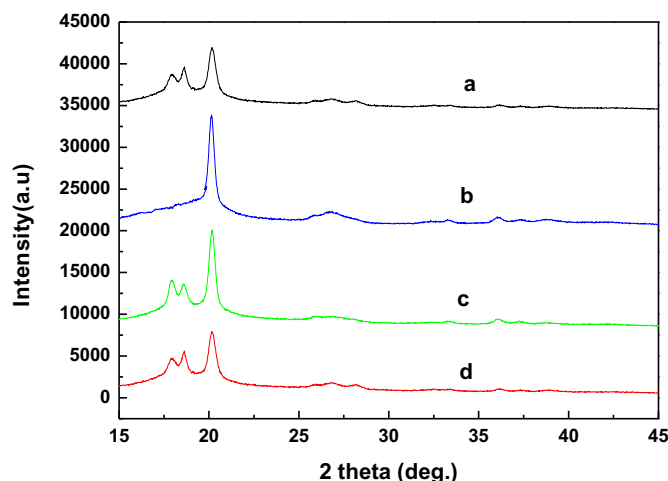
To measure the weight of the electrolyte absorbed by the cathode films, LiCoO<sub>2</sub> cathodes (2.0 × 2.0 cm) were first accurately weighed and immersed in the electrolyte for 24 h. At regular interval, the samples were taken out, pressed lightly between two sheets of clean filter paper to remove surface liquid, and then weighed. The electrolyte uptake of the cathodes increases with increasing the soaking time at the beginning and almost keeps unchanged after soaking for 16 h. The obtained max electrolyte uptakes of the cathode films based on Eq. (1) are shown in Table 1. It can be found from Table 1 that the electrolyte uptake increases with increasing the content of MA-g-PVDF in the MPVDF composite. The improvement in the electrolyte uptakes should be ascribed to the introduction of MA-g-PVDF into PVDF, the former has low crystallinity than the later.

Fig. 1 presents XRD patterns of MA-g-PVDF, PVDF and their blends. PVDF shows one sharp peak at 20.5°, one broad peak at 26.7° and a series of weak peaks between 30° and 40°. Differently, MA-g-PVDF exhibits two additional peaks at 17.9° and 18.6° except for the peaks assigned to PVDF. It can be found that the peak assigned to PVDF becomes much weakened in MA-g-PVDF, suggesting that MA-g-PVDF has low crystallinity than PVDF. Interestingly, when MA-g-PVDF is introduced into PVDF, the diffraction peak of PVDF in the blend becomes weaker and the peak intensity decreases with increasing the content of MA-g-PVDF. This result indicates that the introduction of MA-g-PVDF is able to reduce the crystallinity and to increase the amorphization of PVDF. The amorphous structure of PVDF favors the electrolyte uptake.

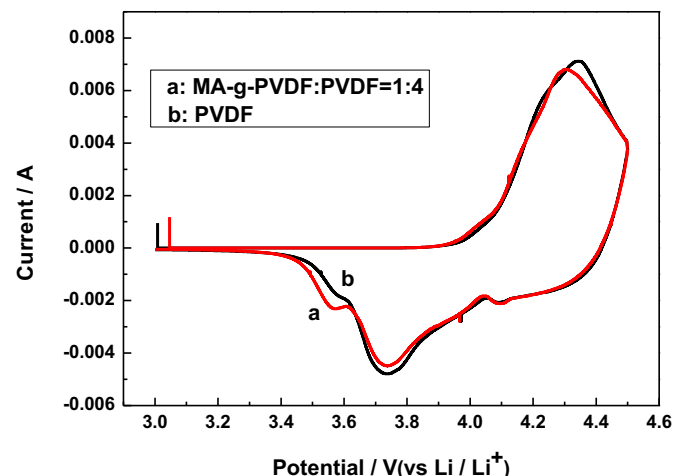
**Table 1**

Electrolyte uptake of LiCoO<sub>2</sub> films and adhesion of the cathode mixture to current collector.

LiCoO <sub>2</sub> cathode	Max electrolyte uptake/%	Adhesion to current collector/N
With PVDF	25.3	1.170
With MA-g-PVDF: PVDF = 1:4	43.5	1.168
With MA-g-PVDF: PVDF = 1:2	45.0	0.492



**Fig. 1.** X-ray diffraction patterns of MA-g-PVDF (a), PVDF (b), the MPVDF (MA-g-PVDF:PVDF = 1:4) (c) and the MPVDF (MA-g-PVDF:PVDF = 1:2) (d).



**Fig. 3.** Cyclic voltammograms of LiCoO<sub>2</sub> electrodes prepared with MPVDF (MA-g-PVDF:PVDF = 1:4) binder (a) and PVDF binder alone (b) in LiCoO<sub>2</sub>/Li cells. Scan step: 0.1 mV s<sup>-1</sup>.

The adhesion strength of the cathode mixture to the current collector (Al foil) obtained by peel test was also shown in Table 1. It can be found that the adhesion strength decreases with increasing the content of MA-g-PVDF in the MPVDF. Obviously, the introduction of MA-g-PVDF decreases the adhesion of PVDF. However, compared to the significant decrease of the adhesion strength for the film made from the composite with the ratio of MA-g-PVDF to PVDF being 1:2 (decreasing from the 1.168 N of the film using PVDF alone to 0.42 N of that using MPVDF), the change from applying the composite with the mass ratio of MA-g-PVDF to PVDF up to 1:4 can be negligible. Thus, the polymer composite binder with a mass ratio of MA-g-PVDF to PVDF = 1:4 was adopted to understand the effect of MA-g-PVDF on the cathode performance.

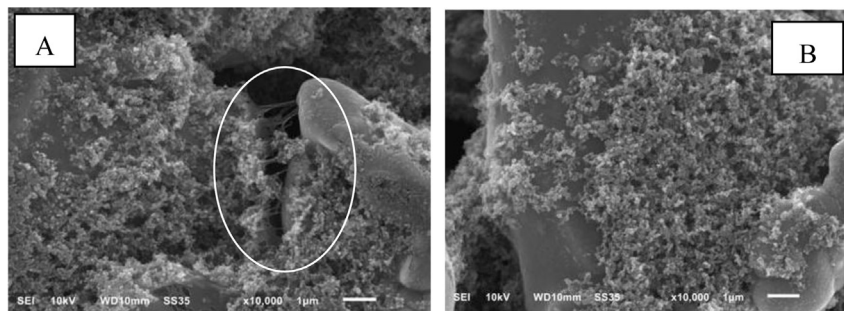
Surface morphologies of the LiCoO<sub>2</sub> electrodes with MPVDF (MA-g-PVDF:PVDF = 1:4) binder and PVDF binder were comparatively observed with scanning electron microscope, and their SEM images are presented in Fig. 2. Differently from the cathode with PVDF alone (Fig. 2B), the cathode with the MPVDF shows gel-like substance in the interspaces among LiCoO<sub>2</sub> particles (as marked with a dashed-circle in Fig. 2A). This substance should result from the introduction of MA-g-PVDF and is responsible for the improvement of electrolyte uptake.

### 3.2. Electrochemical performance

The electrochemical reversibility of two LiCoO<sub>2</sub> electrodes was investigated by cyclic voltammetry. Fig. 3 shows the obtained cyclic voltammograms in LiCoO<sub>2</sub>/Li cells. The shapes of two curves are

similar, indicating that MA-g-PVDF does not participate in the electrochemical reaction in 3.0–4.5 V. The redox peaks for the lithium desertion/insertion in LiCoO<sub>2</sub> can be clearly identified for both electrodes. However, the ratio of anodic peak area to cathodic peak area and the difference between anodic peak potential and cathodic peak potential are different, which are the key indicatives of electrochemical reversibility. The ratio of peak area is 0.928 and 0.912 and the peak potential difference is 567 mV and 655 mV, for the LiCoO<sub>2</sub> electrodes with MPVDF binder and with PVDF binder, respectively, indicating that the former has better electrochemical reversibility. Therefore, the introduction of MA-g-PVDF improves the lithium desertion/insertion kinetics in cathode, which is beneficial for rate capability.

To confirm the improvement of the lithium desertion/insertion kinetics in cathode by the MPVDF, EIS was performed on the fresh LiCoO<sub>2</sub>/Li cells at open circuit voltage. The obtained results are presented in Fig. 4, which are characteristic of a semicircle at high frequencies (representing the interfacial property between electrode and electrolyte) and a slop line at low frequencies (representing the lithium diffusion in cathode). The interfacial resistance can be obtained from the diameter of the semicircle at high frequencies. It is 450 Ω for the LiCoO<sub>2</sub> electrode with MPVDF, while 550 Ω for the electrode with PVDF alone, showing the reduced interfacial resistance of LiCoO<sub>2</sub> electrode by using MPVDF. The reduced interfacial resistance can be ascribed to the better ability of LiCoO<sub>2</sub> electrode to adsorb electrolyte due to the less crystallinity of MPVDF than PVDF.



**Fig. 2.** SEM images of LiCoO<sub>2</sub> electrodes prepared with MPVDF (MA-g-PVDF:PVDF = 1:4) binder (A) and PVDF binder alone (B).

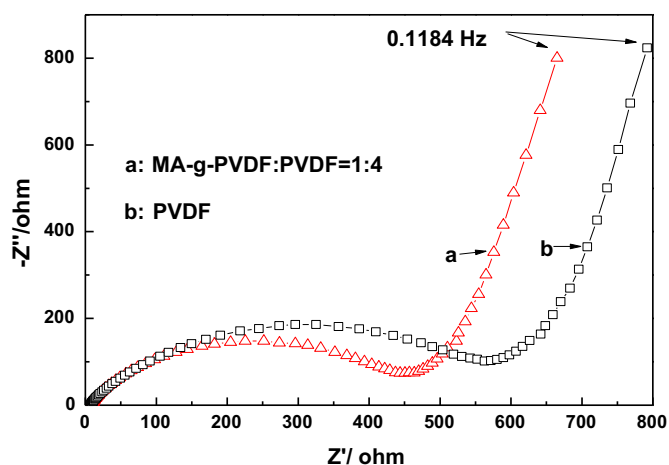


Fig. 4. Nyquist plots of LiCoO<sub>2</sub> electrodes prepared with MPVDF (MA-g-PVDF:PVDF = 1:4) binder (a) and with PVDF binder alone (b) in LiCoO<sub>2</sub>/Li cells.

Fig. 5 shows the discharge curves of LiCoO<sub>2</sub>/Artificial graphite batteries at different current rates according to the LiCoO<sub>2</sub> cathode (0.2 C, 0.5 C, 1.0 C and 2.0 C). It can be seen from Fig. 6 that the batteries can achieve a larger discharge capacity at 0.2 C but the

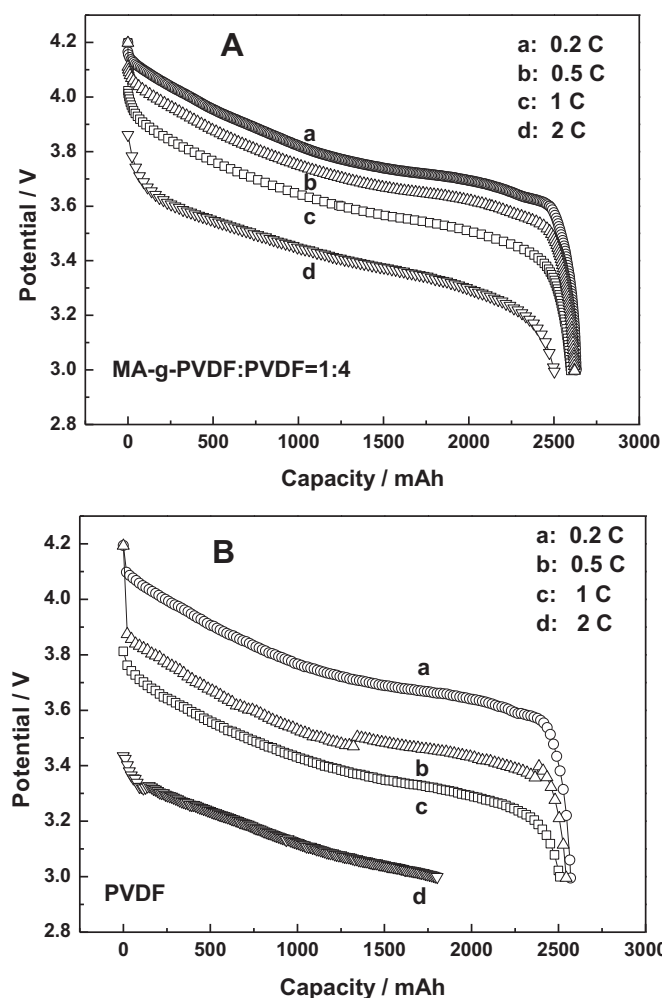


Fig. 5. Rate discharge performance of LiCoO<sub>2</sub>/Artificial graphite batteries. The LiCoO<sub>2</sub> electrodes were prepared with MPVDF (MA-g-PVDF:PVDF = 1:4) binder (A) and with PVDF binder alone (B). The battery was charged at 0.5 C from 3.0 V to 4.2 V and discharged at 0.2 C, 0.5 C, 1.0 C and 2.0 C.

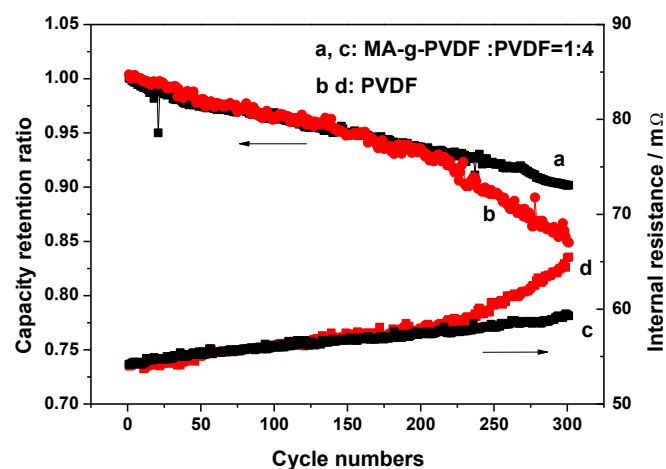


Fig. 6. Variations in capacity retention and internal resistance of LiCoO<sub>2</sub>/Artificial graphite batteries with cycling. The LiCoO<sub>2</sub> electrodes were prepared with MPVDF (MA-g-PVDF:PVDF = 1:4) binder (a and c) and with PVDF binder alone (b and d).

voltage platform and the capacity decreases with increasing discharge current. The discharge capacity is 2.630 Ah, 2.611 Ah, 2.593 Ah and 2.503 Ah for the battery using MPVDF (MA-g-PVDF:PVDF = 1:4), but only 2.580 Ah, 2.552 Ah, 2.506 Ah and 1.807 Ah for the battery using PVDF alone, at 0.2 C, 0.5 C, 1.0 C and 2.0 C, respectively. The discharge capacity of the battery using MPVDF increases by 38.5% at 2.0 C compared to the battery using PVDF alone, showing that the introduction of MA-g-PVDF significantly improves the rate capability of LiCoO<sub>2</sub> battery.

Fig. 6 presents the variation in capacity retention and internal resistance of LiCoO<sub>2</sub>/Artificial graphite with cycling at 0.5 C. It can be seen from Fig. 6 that the battery using MPVDF (MA-g-PVDF:PVDF = 1:4) exhibits better cyclic stability than the battery using PVDF alone. The former keeps 90.2% while the latter keeps only 84.5% of the initial discharge capacity after 300 cycles. Before the 200th cycle the capacity retention of both batteries decreases slightly, but fades quickly for the battery using PVDF alone from 200th cycle, showing the poor cyclic stability of the battery using PVDF. The internal resistance of the batteries is also monitored when it was discharged to 3.0 V in each cycle. The internal resistance of both batteries increases slightly with cycling before 200th cycle. However, the internal resistance of the battery using PVDF alone increases more quickly after 200th cycle than the battery using MPVDF alone. The variation in internal resistance is in well agreement with that in capacity retention. This variation should be related to the lower electrolyte uptake of the cathode using PVDF alone. In the initial cycling, the electrolyte in the cathodes of both batteries is sufficient for the insertion/desertion of lithium ion, and the electrolyte content is not the determining factor for the battery performance. However, after deep cycling, the electrolyte content decreases due to its decomposition, resulting in the deteriorated cyclic stability of the battery. In the case of the battery using PVDF, due to the less electrolyte uptake of the cathode, the electrolyte in the cathode is not sufficient for the insertion/desertion of lithium ion from 200th cycle, resulting in the significantly increased internal resistance and the decayed capacity retention of the battery. Contrastively, the cathode using MPVDF has larger electrolyte uptake and provides the battery with improved performance.

#### 4. Conclusion

A novel polymer composite (MPVDF) as binder for LiCoO<sub>2</sub> cathode of lithium ion battery was developed by embedding maleic anhydride-grated-polyvinylidene fluoride (MA-g-PVDF) into

polyvinylidene fluoride (PVDF). The LiCoO<sub>2</sub>/Artificial graphite battery using MPVDF exhibits improved rate capability and cyclic stability compared to the battery using PVDF alone. The improved performance of the battery is attributed to the low crystallinity of MPVDF, which allows larger electrolyte uptake.

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